Survival of graphitized petrogenic organic carbon through multiple erosional cycles - supplementary material

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Proportion of lithologies in each catchment

Table 1 shows the relative proportion of each lithological group contained in the studied catchments. These proportions were calculated using ArcMap (ESRI). 2-D area percentage was calculated by extracting catchments from a digital elevation model, and generating shapefiles of the area upstream of the sample locations. These were then combined with a geological map shapefile (Chen et al., 2000) and the intersection of catchment and lithology generated new shapefiles. The metadata for these were exported to a table. Two-dimensional areas were extracted from the table and summed for the various lithology groups.

Sample collection

We chose to sample fluvial and marine sediment rather than directly sampling Taiwanese bedrock, for a number of reasons. Firstly, Beyssac et al. (2007) undertook a thorough investigation of the metamorphic rocks of the Hueshuan Range and Central Range, and we do not feel that repeating this work is worthwhile. They collected three transects of bedrock samples, and analysed the CM contained within these using Raman. Secondly, rivers integrate erosional signals from an entire catchment. Sediment samples are more representative of the relative volume of sediment erosion in a catchment compared to a bedrock survey. If a bedrock sampling campaign found a graphite-rich formation, but its contribution to the sediment load in the catchment was negligible, this would bias the characterisation of that river's output. Thirdly, and conversely, if the bedrock survey missed a small but rapidly eroding graphite-rich layer, there may be unexpected graphite exported by the river.

Since Raman spectroscopy analyses individual particles of OC_{petro}, the catchment wide averaging of sediment erosion does not lead to averaging of Raman measurements. Erosively mixed Highly Graphitised and Disordered OC_{petro} will be identified as a bimodal distribution of these two spectral groups.

Samples were collected during by different teams during multiple campaigns. Therefore there is a wide range of sampling techniques and locations used in the study, including sediment coring, manual bedload collection and automated suspended load sampling. We believe that this does not compromise our ability to observe and characterise all available forms of carbonaceous material eroded by the various rivers. Usually, the entire range of gransizes have been collected in one way or another. Laonung samples (LN) include silt through to coarse sand, due to collection from both a fluvial sand bar and fine-grained riverbank material. Gaoping Canyon (CY) cores contained sand and mud sized material, which were both investigated. Gaoping Shelf (SH) sediments only contained mud-sized particles, but we observed the full range of carbonaceous material within these samples. Chenyoulan (CY) material was collected from the suspended load using an autosampler, but since SH samples contained the whole range of carbonaceous material grades, we do not expect systematic loss of any particular type here. Grass Lake Creek was sampled by walking up the semi-dried river bed during the dry season, and sampling cm-scale cobbles of sedimentary rock. These were crushed and ground, which should release and homogenise the samples, allowing all carbonaceous material within to be observed.

Raman spectra collection and fitting

Raman spectra were collected using Renishaw InVia and Ramascope-1000 Raman spectrometers. Dry sediment samples were ground for 12 minutes at 250 rpm in a Retsch PM-400 agate ball-mill grinder. Short-period grinding does not affect Raman charateristics of OC_{petro} (Sparkes et al., 2013). One spatula (~0.25 g) of material was pressed between glass slides to produce a flattened sample area with 2 cm diameter. The process of flattening between slides tends to align graphite flakes with the

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sample surface, meaning that the laser beam is incident perpendicular to the basal planes. Within this area, 10-20 flakes of POC were usually found using a 50 x magnification objective lens. The field of view as rastered across the sample to ensure that no POC flakes were missed.

Measurements were taken using a 514 nm Ar-ion laser, set to between 0.75 and 1.8 mW for 30 seconds to avoid damaging the target. Raman-shift was measured from 800 – 2000 cm^{-1} with an 1800 l mm^{-1} grating. Spectra were fitted using the method described by Sparkes et al. (2013), in which peaks representing the G, D1, D2, D3 and D4 Raman bands were automatically fitted by a computer algorithm. This process allows rapid and objective analysis of a large number of spectra from complex samples. Spectrum metadata (location, height, width and area for each peak, plus peak height and area ratios) was used to classify each sample (Sparkes et al., 2013, 2018). Samples were categorised into "Disordered", "Intermediate", "Mildly Graphitised" and "Highly Graphitised" using a combination of the metamorphic temperature predicted by the "R2" and "RA2" geothermometers of (Beyssac et al., 2002; Lahfid et al., 2010), and the increased width of spectroscopic peaks seen in disordered CM (Sparkes et al., 2013). These geothermometers have been carefully calibrated against metamorphic temperature, using field and laboratory studies (Beyssac et al., 2002, 2003) but show no systematic relationship with pressure. Increased pressures lead to faster graphitization, but not the final degree of graphitization (Beyssac et al., 2003).

Whilst highly graphitised CM can be successfully differentiated using just R2 and the width of the D1 peak, these measurements do not permit separating intermediate and disordered CM. The RA2 calibration of Lahfid et al. (2010), coupled with the combined width of the D1, D2 and G peaks, allows these two groups to be distinguished. The metadata from each spectrum are included as Supplementary Dataset 1, and displayed graphically by plotting the sum of peak widths against the calculated temperature from either the "R2" or "RA2" geothermometers (Figure 2, main paper).

A script implementing the automatic fitting procedure is maintained at `https://github.com/robertsparkes/raman-fitting`

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Table 1: Summary of geological units found in each catchment, grouped by age and stratigraphic section. WF = Western Foothills, HR = Hsueshan Range, CR = Central Range. See also Figure 1.

Sample	Formation							
	Plio-Plei WF	L Mio-Plio WF	M Mio WF	E Mio WF	Eoc-Olig HR	Eoc HR	Eoc CR	Pre-Ter CR
Grass Lake Creek								
CL (coal)	100%	-	-	-	-	-	-	-
SED (sediment)	100%	-	-	-	-	-	-	-
Chenyoulan								
CY	-	1%	38%	23%	11%	27%	-	-
Laonung								
LN	1%	2%	7%	45%	6%	-	38%	1%
Gaoping								
CN (canyon)	3%	10%	16%	36%	5%	1%	27%	1%
SH (shelf)	3%	10%	16%	36%	5%	1%	27%	1%

Table 2: Details of the type and location of samples collected for this study. For full descriptions of all samples except CY, see (Sparkes, 2012)

Sample	Latitude °N	Longitude °E	Date	Type	Method	Water Depth m	Depth in core cm	Grainsize
Grass Lake Coal (CL)	24.08	120.75	2008	Hand specimen	Collected from river bed	N/A	N/A	Cobble size coal clast
Grass Lake Sediment (SED)	24.08	120.75	2008	Hand specimens (7)	Collected from river bed	N/A	N/A	Coarse sandstone
Chenyoulan (CY)								
46B	120.8904	23.5934	2010	Suspended sediment	Autosampler; before flood	N/A	N/A	Unknown
81A	120.8904	23.5934	2010	Suspended sediment	Autosampler; rising limb	N/A	N/A	Unknown
Laonung (LN)								
KP2A	120.5018	22.7976	2009	Bedload	Collected from river bar	N/A	N/A	Coarse sand
KP3B	120.4813	22.7924	2009	Flood sediments	Collected from river bank	N/A	N/A	Fine sand / silt
Gaoping Canyon (CN)								
Core K1	22.4577	120.4142	2009	Box Core	1 cm sub-samples	160	0, 19, 41	Mud above coarsening sand
Core K8X	22.2951	120.2857	2009	Box Core	1 cm sub-samples	749	16	Medium/Fine sand
Core K12	22.4055	120.4085	2009	Box Core	1 cm sub-samples	350	17	Coarse, slaty sand
Gaoping Shelf (SH)								
Core K11	22.2532	120.1763	2009	Box Core	1 cm sub-samples	957	5	Mud
Core L9	22.1840	120.3613	2009	Box Core	1 cm sub-samples	495	0, 5	Mud